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EFFECT OF NONTRADITIONAL ADDITIVES ON THE PROCESSES OF SILICATE AND GLASS FORMATION

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The results of studying the effect of nontraditional additives, namely, metallic aluminum and zinc powders on the process of silicate and glass formation using polythermal and thermogravimetric analysis, are described. The specifics of the glass-melting process for decorative glasses using the nontraditional additives are considered.

Decorite is a special class of decorative opacified glasses for architecture and construction simulating natural marble, jade, or agate [1].

The guiding idea in developing new types of sheet glasses was to have their compositions as standardized as possible, i.e., as close as possible to the composition of industrially made sheet glass and to avoid toxic or scarce opacifying agents. Such compositions should ensure decorative qualities and a high degree of opacification together with good technological properties of glass melt suitable for high-efficiency mechanized technologies, including the float process.

A fundamentally new solution in the synthesis of decorative glasses opacified through liquation due to sulfur sulfide ions is using metal powders as modifying additives.

The production of new types of glasses based on the reference float-glass composition used in the industry and powder metals has certain technological peculiarities, since the decorative and opacifying properties of the glass melt are related to the presence of iron and zinc sulfurous compounds in the melt, whose formation depends on the redox potential of the batch, the sulfide level of the melt, and the technology of synthesis [2].

The sulfidizing mechanism in general can be represented as a scheme (Fig. 1). As sodium sulfate Na_2SO_4 is used as the main sulfur-bearing material, the reducing atmosphere just in the gas furnace is insufficient for the formation of sulfide S^{2-}. It is necessary to have reducing conditions inside the glass melt, since a reducing medium decreases the temperature of the beginning of sulfide formation and increases its yield [3].

Powdered metallic aluminum introduced as a modifying reducing additive creates thermodynamically efficient sulfidizing conditions and provides a high reducing potential of the batch and a reducing melting regime. A significant ad-

vantage of aluminothermic reduction is the exothermic type of the reactions, since oxidation of aluminum is accompanied by a substantial heat release, which is significantly higher than in oxidation of other metals:

$$\frac{2}{m} Me_nO_m + \frac{4}{3} Al \leftrightarrow 2\frac{n}{m} Me + \frac{2}{3} Al_2O_3 + 1584.5 \text{ kJ/mole.}$$
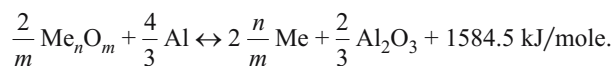
Powdered metallic zinc introduced as the second modifying additive and as the main zinc-bearing component supports the reducing activity of powdered metallic aluminum and thus intensifies the reducing potential of the batch; moreover, having enhanced affinity to sulfur, it increases the sulfide level of the melt, preventing the volatilization and oxidation of sulfur and binding it in a stable compound of zinc sulfide [4].

It is established that only the joint presence of metallic aluminum and zinc powders and sodium sulfate produces marble-like opacification, whereas an increase in the content of the sulfate component changes the degree of opacification from marble-like to opaque milky-white [4].

The purpose of our work is to study the effect of metallic powders on the melting properties of glass melt using the methods of polythermal analysis, thermogravitational analy-
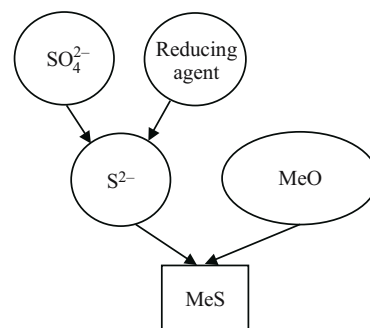

Fig. 1. Mechanism of sulfidizing process.

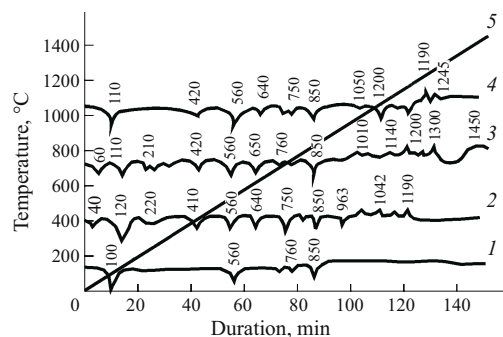[1] Saratov Institute of Glass Joint-Stock Company, Saratov, Russia.

Fig. 2. Derivatographic curves of batches considered: *1*) initial batch; *2*, *3*, and *4*) batches of opacified glasses GS1, GS2, and GS3, respectively; *5*) heating curve.
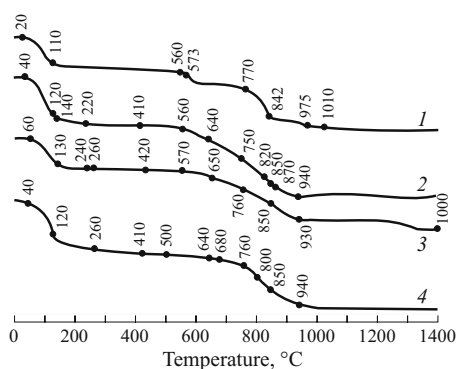

Fig. 3. TG curves of initial (*1*) and experimental batches GS1 (*2*), GS2 (*3*), and GS3 (*4*): *1*, *2*, *3*, and *4*) weight loss 22.5, 27.0, 20.0, and 26.0%, respectively.

sis, IR spectroscopy, rotational viscosimetry and experimental meltings in laboratory and industrial conditions.

For reference purposes we considered the characteristics of clear float glass. The compositions investigated contain different quantities of introduced metals (here and elsewhere wt.%): GS1) 2.40, GS2) 3.0, and GS3) 3.75.

Glass melting is a complicated physicochemical process which proceeds at high temperatures in a moving medium of complex variable composition and depends on the glass composition, heat transfer conditions, temperature, etc.

We have considered two stages of glass melting: silicate and glass formation.

Silicate formation includes different physical processes such as heating of the batch, moisture evaporation, melting of batch components, dissolution of the components in the melt, polymorphic transitions, and volatilization of the components, as well as different chemical processes: dissociation of carbonates, hydrates, nitrates, and sulfates, removal of chemically bound water, reactions between the components, and the formation of silicates. The rate of silicate formation, similarly to any chemical process, depends on the nature and chemical activity of the batch components and their reaction surface. An effective instrument for the process acceleration

is increasing heat transfer to the batch and raising its temperature. In general the first state of melting, i.e., silicate formation, is an endothermic process [5].

An analysis of the thermograms (Fig. 2) obtained on a OD-103 derivatograph (MOM, Hungary) using the polythermal regime in an interval of 20 – 1000°C with a heating rate of 10 K/min indicates that the batches considered have certain additional thermal effects not registered on the DTA curve of the initial batch.
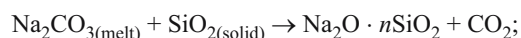
The endothermic effects at the temperatures of 410 – 420 and 640 – 650°C are related to melting of metallic zinc and aluminum, respectively. However, the processes of silicate and glass formation in the initial and experimental batches occur in similar temperature intervals. The IR spectra and diffraction patterns of the experimental batches calcined at 600, 800, and 900°C are identical to those of the initial batch.

However, powder metal particles distributed over the batch volume melt and become oxidized under the effect of high temperatures, transferring heat to the adjacent batch components, thus intensifying their reactions and facilitating an earlier formation of the liquid phase, which is evidenced by the frequency and quantity of thermal effects on the DTA curve of the experimental batches (Fig. 2) and an earlier weight loss increase in the temperature interval of 640 – 760°C. The weight losses in the initial batch are up to 13%, in experimental batches — up to 20% (Fig. 3).

By the end of the silica formation stage the experimental batch constitutes a gray-brown sinter consisting of silicates and silica.

It is seen from the TG curves that silicate formation in experimental batches ends at the temperatures of 930 – 940°C, whereas in the initial batch it end at 980 – 1000°C with the total weight losses in the initial batch up to 22% and in experimental batches up to 27%. This conclusion is corroborated by the polythermic results as well. Analysis of the melting diagrams of the batches considered (Fig. 4) established that, using a 2-hour exposure in the interval of 800 – 1420°C, the glass was completely melted at 1370°C (composition GS3), at 1390°C (composition GS2), and at 1405°C (composition GS1), whereas the reference float glass was completely melted at the temperature of 1420°C.

The bounds of the sintering and silicate formation ranges are shifted by 30 – 40°C toward lower temperatures, and the bounds of glass formation, by 40 – 50°C, compared to float glass. The reactions of silicate and glass formation can be represented in the general form by the following equations:

$$Na_2CO_{3(melt)} + SiO_{2(solid)} \rightarrow Na_2O \cdot nSiO_2 + CO_2;$$

$$Na_2O \cdot nSiO_{2(melt)} + SiO_{2(solid)} \rightarrow Na_2O \cdot SiO_2,$$

where *n* is the content of insoluble SiO_2.

The overall rate of the process is determined by the rate of its slowest stage, which is the dissolution of SiO_2 in the melt [6]. Quartz grains at the stage of glass formation are dissolved in the silicate melt and at the same time silicates are
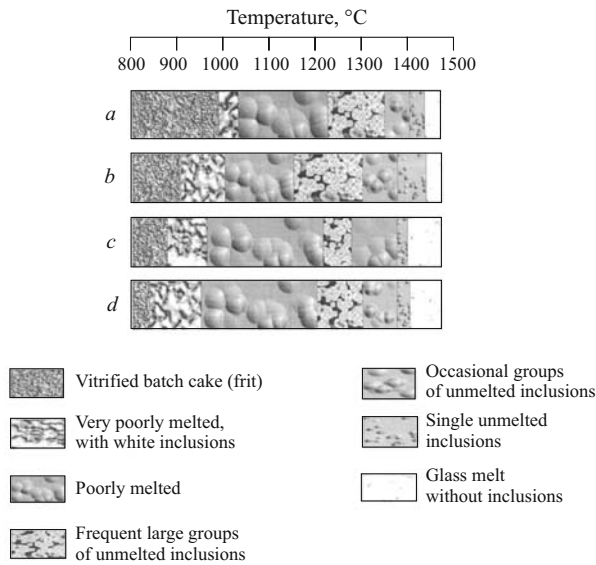
Fig. 4. Melting diagrams of initial (*a*) and experimental GS1 (*b*), GS2 (*c*) and GS3 (*d*) batches.

Fig. 5. Melting duration of experimental batches at temperatures of 1370 (*1*), 1400 (*2*), 1420 (*3*), and 1450°C (*4*).

Fig. 6. Viscosity isotherms of glasses with different content of sulfide sulfur at temperatures of 1250 (*1*), 1350 (*2*), and 1420°C (*3*).

dissolved in each other. By the end of the process the glass melt becomes clear.

The polythermic method makes it possible to obtain a qualitative evaluation of the processes occurring in the batch in heating and to identify the temperature boundaries of the transformation of the batch into melted glass. The Zak – Ponomarev method makes it possible to determine the rate of batch melting or the glass formation rate.

The results of these studies are indicated in Table1. It can be seen that the melting duration of glass batches GS2 and GS3 is virtually identical. The melting of glass GS1 lasts somewhat longer, but yet significantly shorter than that of the initial float glass.

The study of the second stage of the glass melting process in isothermal conditions established a direct dependence of the duration of the complete melting of the batch on its content of metallic additives introduced (Fig. 5). The maximum acceleration of the dissolution of quartz grains is registered in batch GS3 with the maximum content of metallic additives. This composition has the maximum redox potential of the batch and a high content of S^{2-} in the glass melt.

The rate of glass melting as a chemical process is determined by the same factors as the rate of silicate formation, i.e., the compositions of glass and the batch, the reaction surface of grains in the melt, and the temperature conditions, but it also depends on the specifics of the dissolving grains, the properties of the solvent melt, and the rate of its exchange with the dissolving material at contact sites, i.e., on the viscosity and surface tension of the melt [5, 7]. Viscosity is one of the main properties of glass determining its melting conditions. The effect of metal additives on the viscosity of the glass melt is indicated in Fig. 6. It is established that as the concentration of metals added grows, the sulfide level of the melt (Table 1) increases and its viscosity decreases.
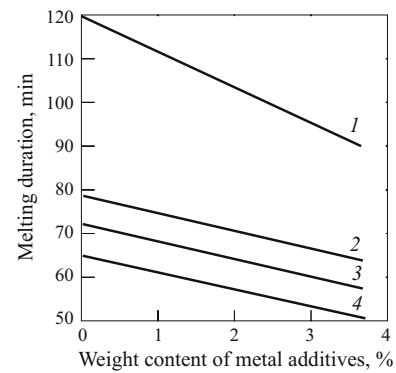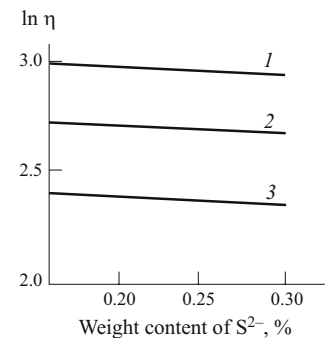
The obtained results can be accounted in the context of the effect of sulfide sulfur as a surfactant. Since the intensity of the dissolution of residual quartz to a large extent is determined by the interphase tension at the quartz grain – melt [8] interface, the emerging capillary-active sulfide sulfur facilitates more intense wetting and penetration of the melt into the depth of the quartz grain causing its disintegration into smaller blocks.

The active release of sulfur dioxide SO_2 in the temperature range of 900 – 1200°C facilitates mixing and intense exchange of the glass melt, which further activates the dissolution of silica grains [9].

For equal quantities of SiO_2, after a 30 min exposure at 1400°C the amount of unmelted material in the initial composition is 30% and in composition GS it is 15%. The melt-

TABLE 1

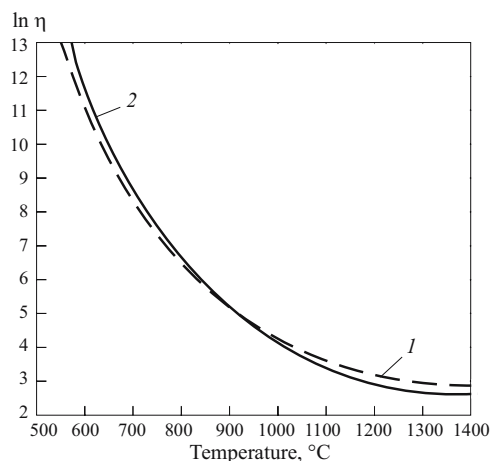| Composition*	Redox potential of batch, mg O^{2-}/100 g batch	Mass content of S^{2-}, %	Duration of glass formation, min
Float glass	20	0.08	78
GS1	80	0.12	70
GS2	147	0.19	68
GS3	160	0.29	68

* Temperature of experiment 1400°C.

Fig. 7. Viscosity characteristics of float glass (*1*) and glass GS (*2*).

ing of batch GS3 requires 10 min less than the melting of the float glass batch.

The comparative viscosity characteristics of the glasses considered are shown in Fig. 7, which can be used to estimate the correlation between the melting properties of the developed opacified glass and the industrial float glass. In the temperature range of 900 – 1300°C the viscosity curve of glass GS is positioned beneath the float glass curve, which shows that glass GS is more fusible.

The results of studying the melting properties of glasses GS were verified in the course of comparative experimental meltings in laboratory furnaces at the maximum temperature of 1420°C with 2 h exposure and in industrial conditions in a batch gas-flame furnace of a capacity of 600 kg of glass melt, at the maximum temperature of 1480°C with 4 h exposure. The obtained glass samples were investigated visually and with a microscope. The glasses GS were clear, amber-colored, well melted and clarified. The obtained glass melt had good opacifying properties (S^{2-} content was 0.17%).

It is known that melting temperature and melting duration are mutually interrelated. Under low melting temperatures (1420°C) the total time of stay of the melt in the furnace increases. At high temperatures (over 1480°C) the glass melt soon loses its opacifying properties, which can be attributed to its decreasing viscosity leading to a more intense exchange between the glass melt layers enriched with sulfide sulfur and sulfate sulfur, as well as volatilization of sulfur in the form of SO_3.

Under a high temperature rise rate and under long exposures within the maximum temperature range sulfide sulfur is partly burned, especially in the surface layers, and the glass melt becomes saturated with a great number of secondary gas bubbles. The degree of opacification in this case sharply decreases. The gaseous atmosphere of the furnace has a significant impact on the sulfide level of the melt. The gaseous atmosphere of the furnace has a perceptible effect on the sulfide level of the melt. Glass melt synthesized in highly reducing or highly oxidizing conditions has weak unstable

opacification. In reducing conditions the rate of oxidation of sulfide sulfur is not high and the glass melt has good opacifying properties (S^{2-} content was 0.17%).

Thus, modifying additives in the form of metallic aluminum and zinc powders introduced into a glass batch due to their melting and exothermic oxidation reactions facilitate an earlier formation of the liquid phase and an active interaction of the batch components in the first stage of glass melting. By developing thermodynamically favorable sulfidizing conditions they ensure a reducing potential in the batch and a high sulfide level in the melt. The presence of sulfide sulfur in a melt decreases the melt viscosity and intensifies the diffusion of the components; the surfactant properties of sulfide sulfur decrease the surface tension of the melt and improve wetting of quartz grains, which accelerates the second stage (glass formation) and generally intensifies the glass-melting process.

The synthesis of opacified glasses using nontraditional additives should be carried out in moderately reducing (neutral) conditions at the maximum melting temperature of 1450 – 1480°C with minimal exposure in the high temperature range. The rate of rise to the maximum temperature should be 30 – 50 K/h.

Based on the obtained results, we can conclude that the melting properties of the proposed opacifying glass composition agree well with the temperature-time conditions of float glass synthesis.

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